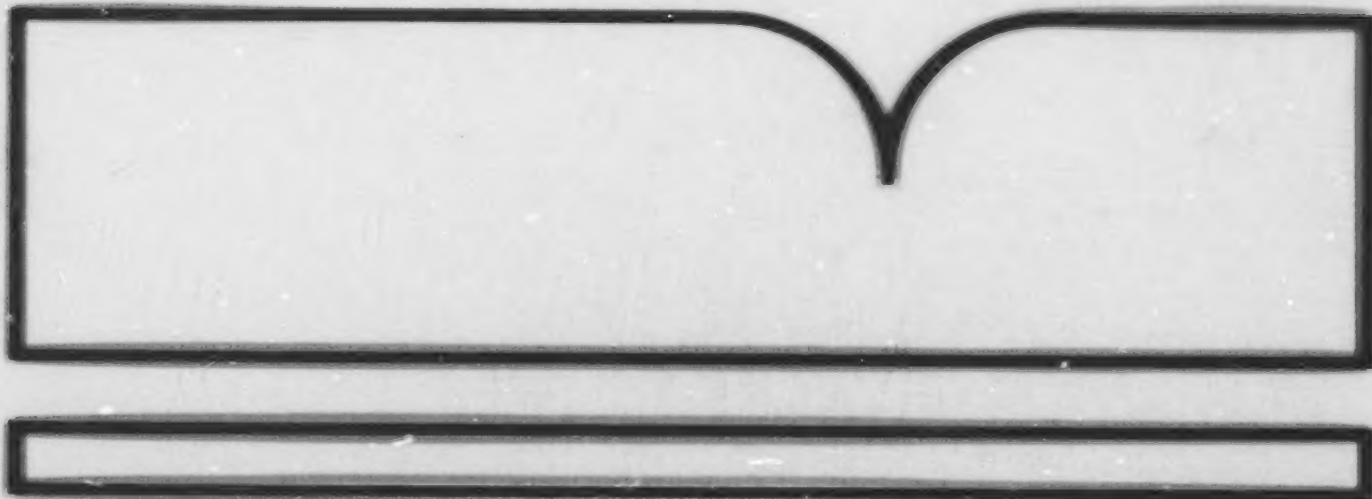


PB88-182209

Summary of the 1986 EPA
(Environmental Protection Agency)
National Performance Audit
Program on Source Measurements

(U.S.) Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Jan 88



U.S. Department of Commerce
National Technical Information Service



United States
Environmental Protection
Agency

Environmental Monitoring
Systems Laboratory
Research Triangle Park NC 27711

EPA/600/4-88-003
January 1988

PB88-182209

Research and Development



A Summary of the 1986 EPA National Performance Audit Program on Source Measurements

A decorative border at the bottom of the page consisting of a series of black and white chevrons pointing to the right.

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA (Please read instructions on the reverse before completing)		
1. REPORT NO. EPA/600/4-88/003	2.	3. RECIPIENT'S ACCESSION NO. PB88- 182209
4. TITLE AND SUBTITLE A Summary of the 1986 EPA National Performance Audit Program on Source Measurements		5. REPORT DATE January 1988
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) E.W. Streib and W.J. Mitchell		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency Office of Research and Development Environmental Monitoring Systems Laboratory Quality Assurance Division (MD-77B) Research Triangle Park, NC 27711		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency Office of Research and Development Environmental Monitoring Systems Laboratory Quality Assurance Division (MD-77B) Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final
		14. SPONSORING AGENCY CODE EPA-600/08
15. SUPPLEMENTARY NOTES		
16. ABSTRACT In 1986, the Quality Assurance Division conducted the National Audits for Stationary Source Test Methods. The audit materials consisted of: a disposable gas cylinder for Method 3 (Orsat analyzer), a calibrated orifice for Method 5 (DGM only), five simulated liquid samples each for Method 6 (SO₂) and Method 7 (NO_x), and two coal samples for Method 19. Participating laboratories sent their data to the Source Branch and in return received a written report comparing their results to EPA's. In the Method 3 audit, each parameter had only one concentration. The mean for CO₂ was 3.7% from the expected (EPA) value. The mean for O₂ was 0.4%. In the Method 5 audit, the mean value for all participants differed by 3.9% from the expected value. For the Method 6 audit, the average mean differed by 2.0% from the expected value, and in the Method 7 audit, the average mean differed by 5.0%. In the two coal audits, the parameters measured were sulfur, moisture, ash, and Btu content. On the average, for the sulfur analysis, 90% of the participants measured within 10% of the expected value; for Btu, 99% of the participants measured within 10% of the expected value.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT Unrestricted	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 43
	20. SECURITY CLASS (This page) Unclassified	22. PRICE AD3 12.95

EPA/600/4-88/003
January 1988

A SUMMARY OF THE 1986 EPA NATIONAL PERFORMANCE AUDIT PROGRAM
ON SOURCE MEASUREMENTS

by

E. W. Streib and W. J. Mitchell
Quality Assurance Division
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

DISCLAIMER

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the environment, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection regulations through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of Agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Environmental Protection Agency, including the Office of Air and Radiation and the Office of Toxic Substances.

The major task of this study was to report the results of the national quality assurance audit program for stationary source test methods. Audits were designed to estimate the minimal analytical and computational accuracy that can be expected with Method 3 (carbon dioxide and oxygen), Method 5 (dry gas meter only), Method 6 (sulfur dioxide), Method 7 (nitrogen oxides), and Method 19 (coal). Statistical analysis was used to characterize the data.

James W. Falco, Director
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina

ABSTRACT

In 1986, the Quality Assurance Division conducted the National Audits for Stationary Source Test Methods. The audit materials consisted of: a disposable gas cylinder for Method 3 (Orsat analyzer), a calibrated orifice for Method 5 (dry gas meter only), five simulated liquid samples each for Method 6 (SO₂) and Method 7 (NO_x), and two coal samples for Method 19. Participating laboratories sent their data to the Source Branch and in return received a written report comparing their results to EPA's.

In the Method 3 audit, each gas component had only one concentration. The mean CO₂ value for all participants differed by 3.7 percent from the expected (EPA) value, and the mean for O₂ was 0.4 percent from the expected value.

In the Method 5 audit, the mean value for all participants differed by 3.9 percent from the expected value. For the Method 6 audit, the average mean differed by 1.5 percent from the expected value. The average mean in the Method 7 audit was 6.3 percent from the expected value.

In the two coal audits, the parameters measured were sulfur, moisture, ash, and Btu content. On the average for the sulfur analysis, 91 percent of the participants measured within 10 percent of the expected value; for Btu, 99 percent of the participants measured within 10 percent of the expected value.

This report includes the results of the performance audits done during the period from January to December 1986.

CONTENTS

	<u>Page</u>
Foreword	iii
Abstract	iv
Figures	vi
Tables	vii
Acknowledgment	ix
1. Introduction	1
2. Summary	2
3. Method 3 Audit	6
4. Method 5 Dry Gas Meter Audit	8
5. Method 6 Audit	13
6. Method 7 Audit	17
7. Method 19 Audit	21
References	25
Appendix	26

FIGURES

<u>Number</u>		<u>Page</u>
1	Cumulative accuracy for participants in Method 5 audit, 0686	10
2	Previous results of Method 5 audit	11
3	Results of Method 5 audit, 0686	12
4	SO ₂ expected values compared to participants' values	15
5	Percent difference of mean values and confidence intervals from expected values.....	16
6	NO _x expected values compared to participants' values	19
7	Percent difference of mean values and confidence intervals from expected values.....	20

TABLES

<u>Number</u>		<u>Page</u>
1	Participants' Results from Method 3 Audit (All Data--No Outliers Removed)	2
2	Method 5 Audit - Summary Statistics	3
3	Participants' Results from Methods 6 and 7 Audits (All Data--No Outliers Removed)	3
4	Participants' Results from Methods 6 and 7 Audits (Outliers Removed)	4
5	Participants' Results from Method 19 Coal Audits (All Data--No Outliers Removed)	5
6	Method 3 Audit Participants	6
7	Source Method 3 Audit	7
8	Method 5 Audit Participants	8
9	Results of Method 5 Audit, 1982-1986	9
10	Method 6 Audit Participants	13
11	Summary of Source SO ₂ Audit	14
12	Method 7 Audit Participants	17
13	Summary of Source NO _x Audit	18
14	Coal Audit Participants	22
15	Source Coal Audit--0386	23
16	Source Coal Audit--0986	24
17	National Orsat Audit Frequency Distribution of Absolute Percent Differences of Expected and Reported Values	27
18	DGM Frequency Distribution of Absolute Percent Difference	28

TABLES (Continued)

<u>Number</u>		<u>Page</u>
19	SO ₂ Frequency Distribution of Percent Difference--No Outliers Removed	29
20	NO _x Frequency Distribution of Percent Difference--No Outliers Removed	29
21	National Coal Audit Frequency Distribution of Absolute Percent Differences of Expected and Reported Values-- Study 0386	30
22	National Coal Audit Frequency Distribution of Absolute Percent Differences of Expected and Reported Values-- Study 0986	31

ACKNOWLEDGMENT

We express our appreciation to the laboratories that participated in the National Performance Audit Program for Stationary Sources. Thanks also to the staff of the Standards Laboratory/Performance Evaluation Branch/Environmental Monitoring Systems Laboratory (EMSL), who did the acceptance testing of the audit samples, and to the programmers of the Monitoring and Assessment Division/EMSL for providing the data systems to store and evaluate the data.

SECTION 1

INTRODUCTION

The Environmental Protection Agency's (EPA's) Environmental Monitoring Systems Laboratory (EMSL) at Research Triangle Park, North Carolina, established an audit program in 1977 to evaluate the performance of companies that conduct compliance testing using EPA reference methods. The audits check the participants' analytical accuracy in applying the analytical phase of EPA Reference Methods 3, 6, 7, and 19 and the calibration accuracy of the Method 5 control console.⁽¹⁾ Accuracy is defined as the percent difference between a participant's analytical results and the EPA expected value. By participating in this free and voluntary program, testing companies can compare their performance to the performance of other laboratories conducting similar measurements.

Source Test Methods 3, 5, 6, and 7 were each audited once, and Method 19 was audited twice in 1986. Each participating laboratory received an audit package consisting of the audit sample, a data card, instructions, and an envelope for returning the data to EPA. A label for returning the audit device was included with the Method 5 audit package. Participants had 8 weeks to use the audit material and return their data to EPA. At the end of this period, all data received were statistically analyzed to determine the accuracy with respect to the EPA expected value and those obtained by the participants (see Appendix).

The Quality Assurance Division of EMSL also maintains a limited repository of samples for EPA Methods 3, 6, 7, and 19 that are available to source testing laboratories for purposes such as training new personnel or conducting quality control checks. Because the expected values for these samples are included with the analysis instructions, there is no requirement for the data to be returned to EPA. We recommend that source testing laboratories use this sample repository to help improve their overall analytical performance.

This report summarizes the results obtained in the 1986 source audits.

SECTION 2

SUMMARY

In 1986, EPA's EMSL at Research Triangle Park, North Carolina, conducted National Quality Assurance Audits for Stationary Source Test Methods 3 (Orsat analyzer), 5 (dry gas meter only), 6 (SO₂), 7 (NO_x), and 19 (coal). Industrial laboratories, contractors, foreign laboratories, as well as local, state, and federal agencies, participated.

The results of the 1986 audit of Method 3 are summarized in Table 1. Participants analyzed the gas sample twice for percentages of carbon dioxide (CO₂), oxygen (O₂), and carbon monoxide (CO). The mean values of CO₂ and O₂ differed by 3.7 percent and 0.4 percent from the expected values, respectively. The mean values for CO differed only by 4 percent from the expected values.

TABLE 1. PARTICIPANTS' RESULTS FROM METHOD 3 AUDIT
(ALL DATA--NO OUTLIERS REMOVED)

Type of sample	Parameter	No. of analyses	Repl-icate	EPA true value	Participant results		
					Mean	Median	Std. dev.
Small cylinder (gas)	% CO ₂	56	1	6.00	5.80	5.80	0.75
		55	2	6.00	5.78	5.80	0.69
	% O ₂	56	1	10.00	10.03	10.00	0.68
		55	2	10.00	10.04	10.00	0.74
	% CO	37	1	10.00	9.61	9.20	2.10
		36	2	10.00	9.60	9.20	2.13

One audit of Method 5 was conducted in 1986. The overall results (no outliers removed) are summarized in Table 2. The mean for all participants was 3.9 percent from the expected value, and the standard deviation was 7.7 percent. After the removal of 5 percent of the data to eliminate statistical outliers, the mean was 2.8 percent from the expected values and the standard deviation was 2.2 percent. The participants' performance based on the standard deviation of all data was good and consistent with previous years. (2,3,4,5)

TABLE 2. METHOD 5 AUDIT - SUMMARY STATISTICS

	n	Mean %	Median %	Std dev. %
All data	552	3.9	2.5	7.7
Outliers removed	526	2.8	2.4	2.2

Table 3 represents the data (no outliers removed) from the Methods 6 and 7 audits. In the Method 6 audit, the procedure requires the participants to determine the sulfate content in five aqueous solutions using the titration procedure. For all five concentrations, the mean of the combined participants' results was less than 2 percent from the expected value, and the median differed by less than 1 percent. In the Method 6 Audit, 82 to 89 percent of the participants achieved an accuracy within 5 percent of the expected value.

The Method 7 audit procedure requires that the participants determine the nitrate content in five aqueous solutions. For four of the five concentrations, the mean of the combined participants' results was less than 5 percent from the expected value, and the median differed by 3 percent. In this audit, 70 percent of the participants achieved an accuracy within 10 percent of the expected value for four out of five concentrations.

TABLE 3. PARTICIPANTS' RESULTS FROM METHODS 6 AND 7 AUDITS
(ALL DATA--NO OUTLIERS REMOVED)

Type of sample	No. of analyses	EPA true value (mg/DSCM)	Participant results		
			Mean	Median	Std. dev.
Aqueous sulfate	90	350.8	356.1	350.0	52.5
	92	846.5	853.4	844.9	85.1
	91	907.5	903.3	904.3	95.5
	93	1151.5	1148.3	1142.4	85.1
	91	1227.8	1225.9	1217.0	190.6
Aqueous nitrate	70	130.0	124.9	129.0	32.5
	69	350.0	327.9	348.8	72.0
	70	390.0	374.5	388.0	72.4
	70	555.0	529.7	557.0	120.4
	67	620.0	596.9	636.0	169.4

Table 4 represents the data from Methods 6 and 7 after the removal of outliers. Four percent of the Method 6 data and 6 percent of the Method 7 data were classified as outliers. However, even before the statistical outliers were removed, a great improvement was seen in this year's Method 6 data (based on the standard deviation) over last year's data.⁽⁵⁾

TABLE 4. PARTICIPANTS' RESULTS FROM METHODS 6 AND 7 AUDITS
(OUTLIERS REMOVED)

Type of sample	No. of analyses	EPA true value (mg/DSCM)	Participant results		
			Mean	Median	Std. dev.
Aqueous sulfate	88	350.8	349.6	349.9	21.9
	90	846.5	842.7	844.5	35.2
	89	907.5	901.6	904.3	51.0
	89	1151.5	1138.4	1142.0	36.9
	88	1227.8	1217.9	1216.7	60.3
Aqueous nitrate	67	130.0	126.1	129.2	20.7
	67	350.0	335.9	348.9	54.5
	67	390.0	380.3	389.0	44.7
	69	555.0	537.3	557.0	102.8
	63	620.0	615.5	638.6	106.8

Table 5 summarizes the results of the two coal audits that were conducted in 1986. Participants analyzed each coal sample in duplicate for percentages of sulfur, moisture, and ash, and for gross calorific value (Btu/lb). The means of the combined ash and combined sulfur contents were within 10 percent of the expected value; whereas, moisture values differed by as much as 37 percent. An accuracy of one percent was achieved on the mean of combined Btu content. The Btu content as measured by the participants is lower than the EPA value because coal oxidation is not prevented in the audit sample. The Btu content results are a good example of the accuracy with which a measurement can be made when that measurement receives good laboratory quality control.

TABLE 5. PARTICIPANTS' RESULTS FROM METHOD 19 COAL AUDITS
(ALL DATA--NO OUTLIERS REMOVED)

Audit date	Parameter	No. of analyses	EPA value	Participant results		
				Mean	Median	Std. dev.
0386	% S	130	1.72	1.78	1.70	0.88
0986		135	1.26	1.39	1.30	0.74
0386		130	3.54	3.51	3.53	0.25
0986		135	3.02	3.00	2.99	0.25
0386	% H ₂ O	131	1.04	1.06	1.08	0.26
0986		135	1.89	2.59	1.84	8.24
0386		131	3.93	3.54	3.58	0.52
0986		135	2.11	2.80	2.08	8.19
0386	% Ash	130	11.65	11.69	11.65	0.33
0986		134	9.73	9.63	9.61	0.31
0386		130	17.17	17.03	17.06	0.27
0986		134	12.29	12.20	12.27	0.87
0386	Btu/lb	126	12412.0	12299.2	12326.5	201.4
0986		131	13271.0	13243.2	13266.0	196.6
0386		126	13684.0	13633.4	13658.5	144.0
0986		131	13578.0	13553.3	13576.0	132.7

SECTION 3

METHOD 3 AUDIT

The Method 3 audit checks the participants' abilities to analyze a gas sample using an Orsat analyzer. The audit package consists of a disposable cylinder that contains a 4-liter (L) sample of CO₂, O₂, and CO. The analyst expels the gas into the Orsat analyzer using the positive pressure of the cylinder. The gas sample is quantitatively analyzed for percentage of CO₂, O₂, and CO.

In the 1986 audit, 55 percent of the 93 laboratories receiving the audit package returned data. Table 6 shows the total number of laboratories requesting participation and the number that returned data for the Method 3 audit.

TABLE 6. METHOD 3 AUDIT PARTICIPANTS

Category	No. receiving samples	No. returning data
Contractors	50	24
Industry	25	15
Foreign	2	2
Federal	2	1
State	11	6
Local	3	3
Total	93	51

Table 7 summarizes the Method 3 audit results. Each laboratory was asked to analyze the sample in duplicate. Five and ten percent accuracies were chosen for the reporting criteria for each of the parameters. Each parameter had only one concentration.

In the 1986 audit, 64 percent of the reporting laboratories achieved an accuracy within 5 percent for the CO₂, which was an increase from the last audit.⁽⁵⁾ Eighty-five percent of the laboratories achieved an accuracy within 5 percent of the expected value for the O₂ analysis. For the CO analysis, only 30 percent of the laboratories achieved an accuracy within 5 percent, and 34 percent of the laboratories did not report a value for CO.

TABLE 7. SOURCE METHOD 3 AUDIT

Expected value	No. of analyses*	Laboratories accurate within 5% (%)	Laboratories accurate within 10% (%)
6.00	(1) 56	61	89
	(2) 55	64	87
10.00	(1) 56	82	96
	(2) 55	85	91
10.00	(1) 37	32	70
	(2) 36	28	69

*Numbers in parentheses indicate first and second analyses.

SECTION 4

METHOD 5 DRY GAS METER AUDIT

In the Method 5 audit procedure, participants use a calibrated orifice to check the calibration of the dry gas meter in their EPA Method 5 control console (meter box). They insert the orifice in the Method 5 meter box, allow the box to warm up, and then make three 15-min volume measurements. The participants convert each of the three volumes to cubic meters at standard conditions using the formula specified in Eq. 5.1 of Method 5 (Appendix A, 40 CFR 60) and record them on the data card. Then they return the orifice and the data card to EPA, where the data undergoes statistical analysis.

In the 1986 audit, 63 percent of the 141 laboratories that received the audit package returned data. Table 8 shows the categories of participants, the number of participants who requested participation in the Method 5 audit, and the number who actually returned data.

TABLE 8. METHOD 5 AUDIT PARTICIPANTS

Category	No. receiving samples	No. returning data
Contractors	74	38
Industry	41	30
Foreign	6	5
Federal	2	2
State	13	9
Local	5	4
Total	141	88

Figure 1, a cumulative histogram, shows the accuracy obtained by participants in the Method 5 audit, expressed as the percent difference from the expected (EPA) value at various levels of accuracy. The Code of Federal Regulations⁽¹⁾ requires that the dry gas meter be calibrated within an accuracy of 2 percent. Figure 2 shows that 41 percent of the reporting laboratories attained this accuracy. Table 9 summarizes Method 5 audits from 1982 to 1986 and shows an improvement in the mean value and standard deviation.

TABLE 9. RESULTS OF METHOD 5 AUDIT, 1982-1986

Audit	Number of analyses	Mean (% from EPA value)	Median	Std. dev.
0382	827	7.6	2.5	39.5
0982	769	12.5	2.5	81.4
0383	763	5.7	2.2	32.7
0983	614	4.1	1.9	21.3
0684	631	3.1	1.9	4.9
0685	633	10.6	2.2	102.1
0686	552	3.9	2.5	7.7

The histogram in Figure 3 depicts the individual results from all participants of the 1986 audit and includes the mean and median values. Most laboratories reported values higher than the EPA value.

The standard deviation of each laboratory's triplicate analysis (repeatability) indicated that 76 percent of the standard deviations for each set were within 0.3 percent. Four percent of the 1986 data were identified as outliers using Chauvenet's Criterion.⁽⁶⁾ Before the outliers were removed, the mean value (absolute) differed by 3.9 percent from the expected value. After deletion of outliers, this value was reduced to 2.8 percent.

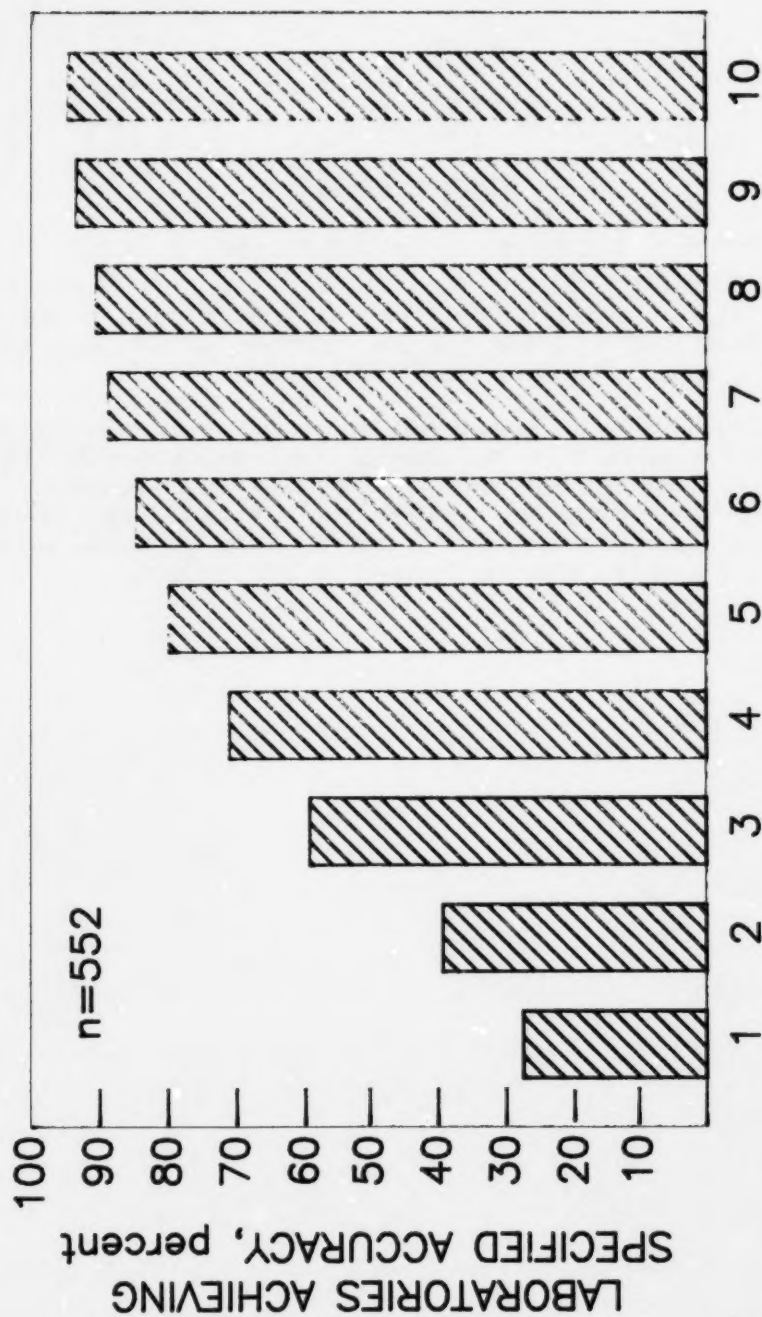


Figure 1. Cumulative accuracy for participants in Method 5 audit, 0686.

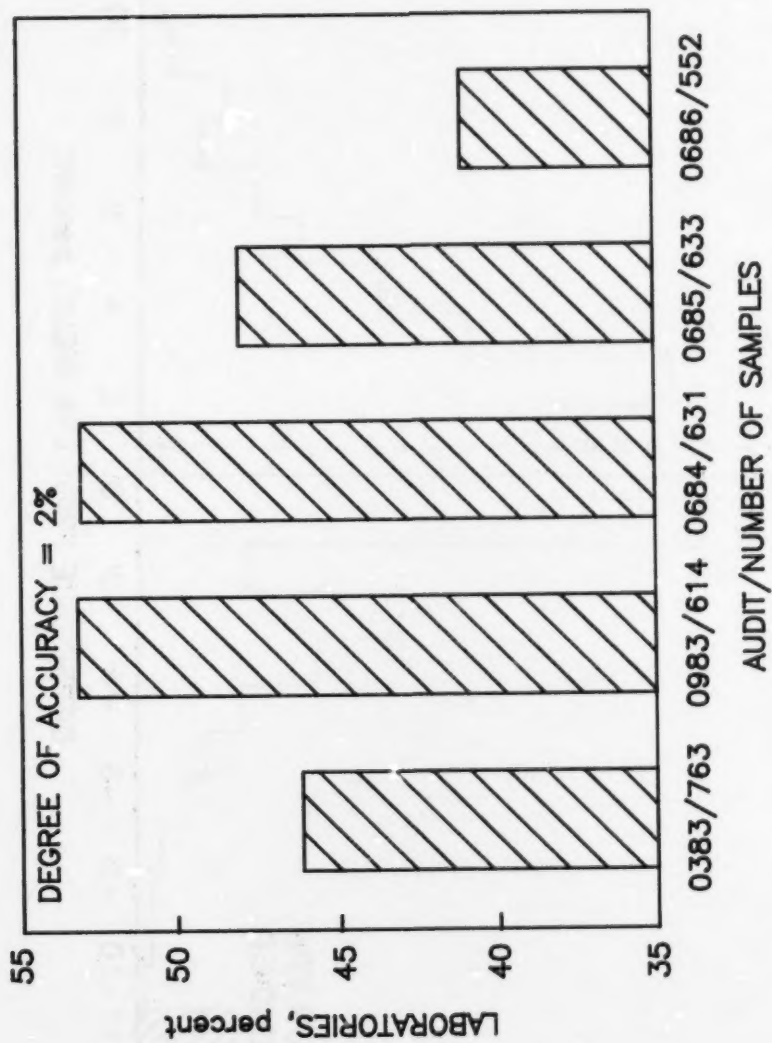


Figure 2. Previous results of Method 5 audit.

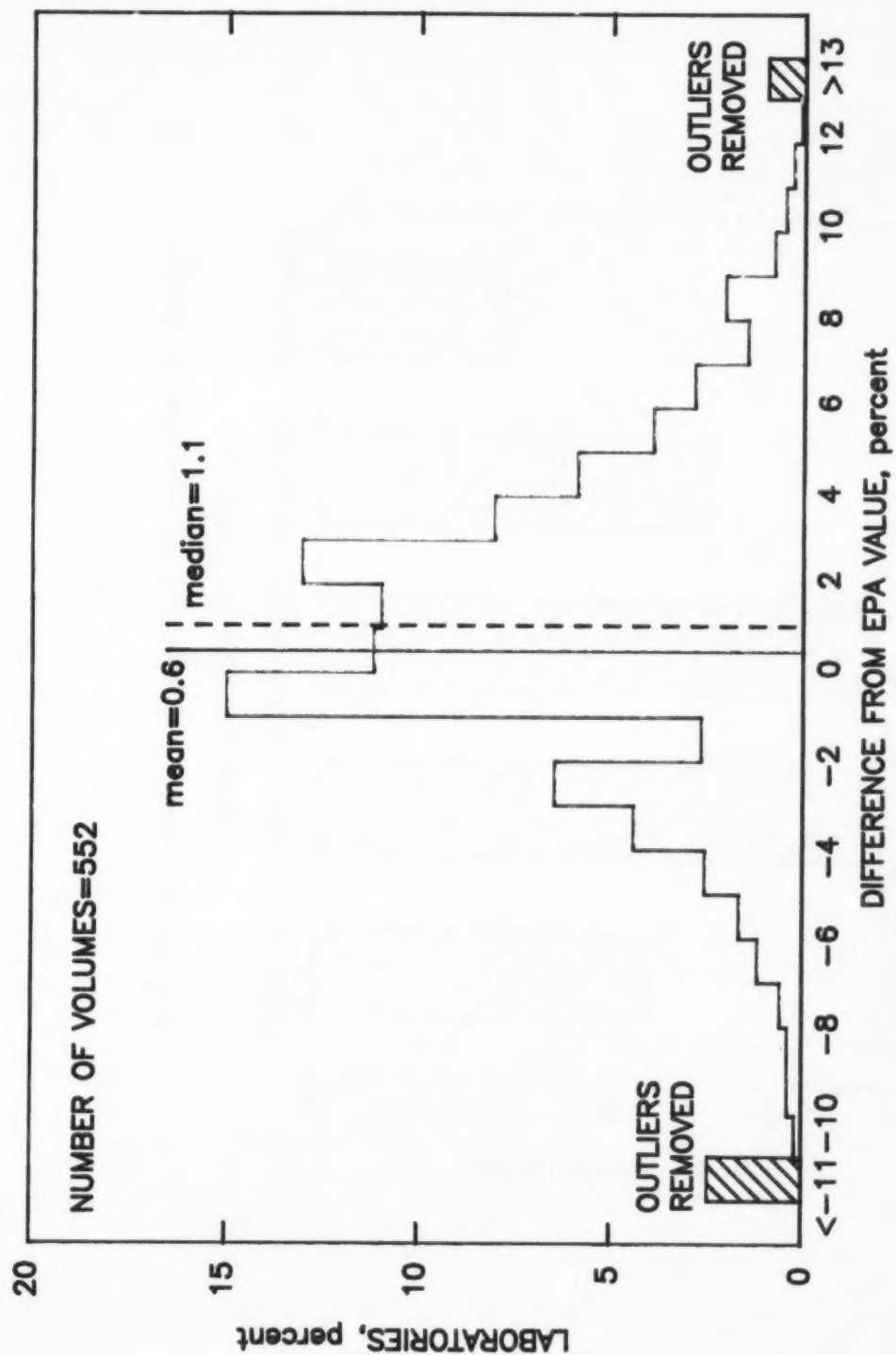


Figure 3. Results of Method 5 audit, 0686

SECTION 5

METHOD 6 AUDIT

The Method 6 audit checks the participants' abilities to quantitatively analyze Method 6 samples for sulfur dioxide content. The audit set consists of five aqueous dilutions of 10 N sulfuric acid in 25-milliliter (mL) sealed glass ampoules. The analyst withdraws 5 mL from each ampoule, adds 30 mL of 3 percent hydrogen peroxide, and dilutes this sample to 100 mL with distilled water. A 20-mL aliquot is then withdrawn from the diluted sample, 80 mL of 100 percent isopropanol and thorin indicator are added, and the sample is titrated with barium perchlorate to a pink endpoint. In calculating the results, the participants assume an original liquid sample volume of 100 mL and a gas sample volume of 0.021 dry standard cubic meter (DSCM) of stack gas.

Table 10 shows the categories of the participants and compares the total number of participants requesting participation with the number returning data. In the 1986 audit, 68 percent of the 137 laboratories that received the audit package returned data.

TABLE 10. METHOD 6 AUDIT PARTICIPANTS

Category	No. receiving samples	No. returning data
Contractors	72	44
Industry	41	31
Foreign	5	3
Federal	1	0
State	11	9
Local	7	6
Total	137	93

Table 11 shows the percentage of laboratories that achieved 2 percent and 5 percent accuracy for each of the five different concentrations in the Method 6 audit. At least 81 percent of the reporting laboratories achieved an accuracy within 5 percent for all five concentrations. Five percent is used as the criterion because it was established as the criterion for source SO₂ compliance audit samples (Section 4.4 of Method 6).

TABLE 11. SUMMARY OF SOURCE SO₂ AUDITS

Concentration (mg/DSCM)	±5 (% of laboratories)	±10% (% of laboratories)
350.8	81.1	88.9
846.5	89.1	93.5
907.5	85.7	93.4
1151.5	88.2	94.6
1227.8	87.9	92.3
N	93	

Figure 4 shows the mean values for each SO₂ concentration and the confidence intervals (CI). Each CI is calculated using the 95 percent confidence level. Figure 5 shows that the mean values and the CI's are within the 5 percent criterion. Overall, the SO₂ audit with its smaller standard deviation showed great improvement from last year's audit.⁽⁵⁾

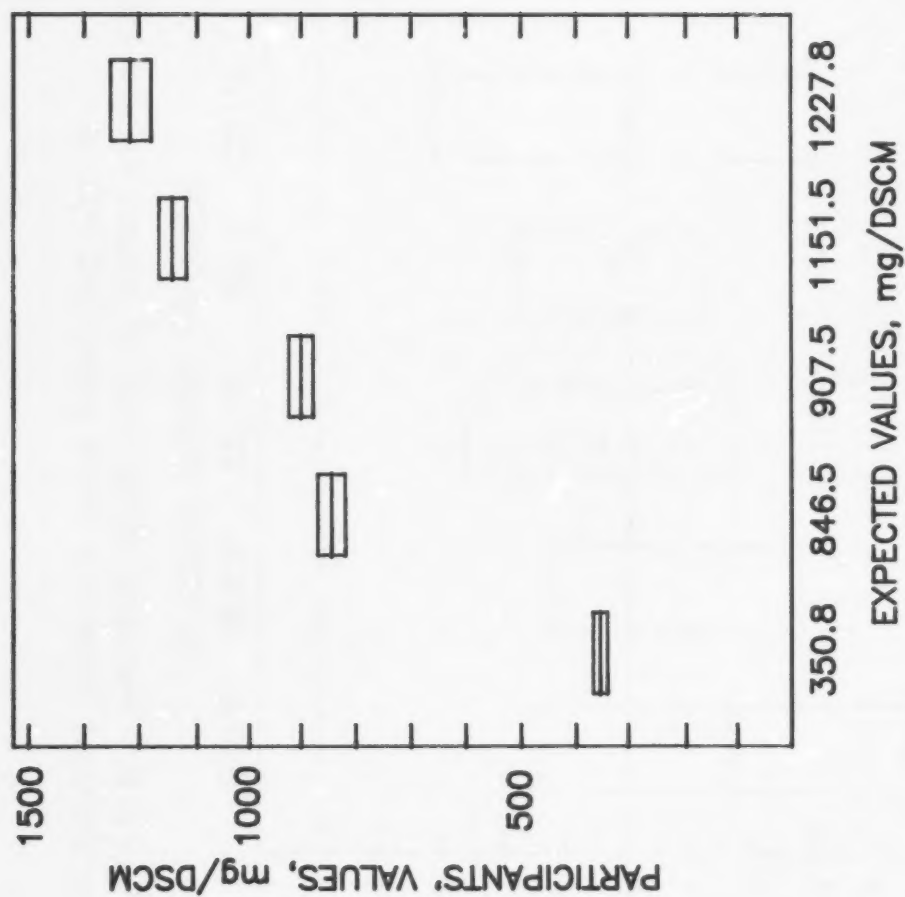


Figure 4. SO₂ expected values compared to participants' values.

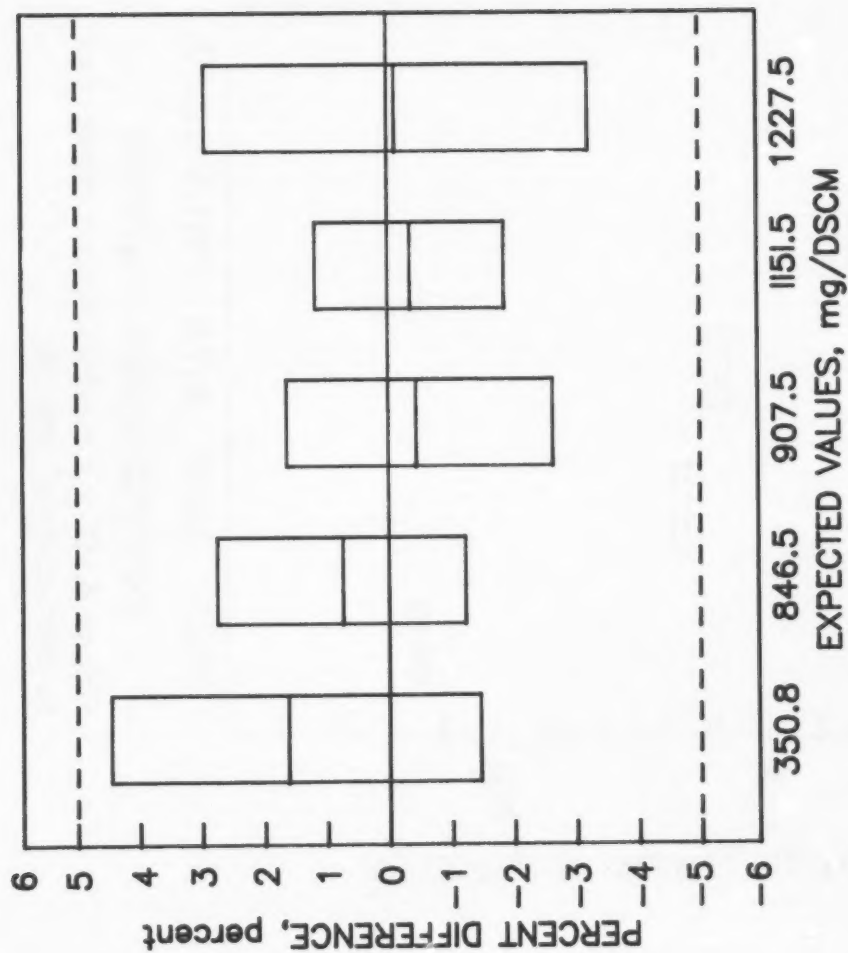


Figure 5. Percent difference of mean values and confidence intervals from expected values.

SECTION 6

METHOD 7 AUDIT

The Method 7 audit checks the participants' ability to quantitatively analyze Method 7 samples for nitrate content. The NO_x audit set consists of five aqueous dilutions of a potassium nitrate solution in 25-mL glass ampoules that are autoclaved after sealing so that bacteria that might attack the nitrate are destroyed. The analyst withdraws 5 mL of solution from an ampoule, adds this with 25 mL of Method 7 absorbing solution to a flask, adjusts the pH with sodium hydroxide, and dilutes to 50 mL with distilled water. A 25-mL aliquot is withdrawn from the diluted sample, placed in an evaporating dish, and analyzed as described in Section 4.3 of Method 7.⁽¹⁾ After this treatment is completed, the absorbance is measured at 410 nanometers (nm) with a calibrated spectrophotometer. In calculating the concentrations present, the participant assumes that 2000 mL of stack gas was sampled.

Table 12 shows the total number of laboratories requesting participation and the number that returned data for the 1986 Method 7 audit. Sixty-four percent of the 110 laboratories receiving the audit package returned data.

TABLE 12. METHOD 7 AUDIT PARTICIPANTS

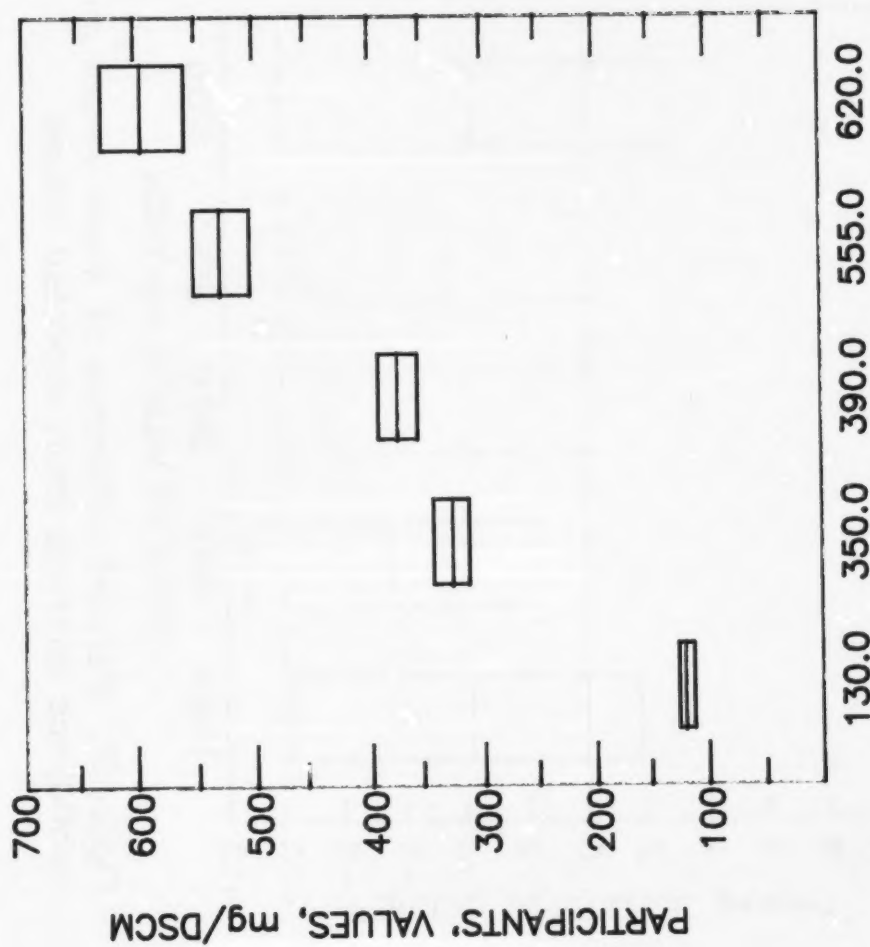
Category	No. receiving samples	No. returning data
Contractors	63	36
Industry	33	22
Foreign	2	2
Federal	1	0
State	5	5
Local	6	5
Total	110	70

The percentage of laboratories that achieved 10 and 20 percent accuracy for each of the five concentrations is shown in Table 13. Ten percent is used as the criterion because it was established as the criterion for the source NO_x compliance audit samples (Section 4.4 of Method 7). Fifty-seven percent of the reporting laboratories achieved an accuracy within 10 percent on the lowest concentration, and 74 percent achieved an accuracy within 10 percent on the highest concentrations.

TABLE 13. SUMMARY OF SOURCE NO_x AUDIT

Concentration (mg/DSCM)	±10% (% of laboratories)	±20% (% of laboratories)
130.0	57.2	78.6
350.0	71.0	87.0
390.0	74.3	90.0
555.0	70.0	85.7
620.0	74.6	83.6
N	70	

Figure 6 shows the means for each NO_x concentration and the CIs. The CIs are calculated in the same way as they were for SO₂. Figure 7 shows that all mean values were lower than the true values. The standard deviations for NO_x were low which accounts for the narrow (±6.8%) CI.



EXPECTED VALUES, mg/DSCM

Figure 6. NO_x expected values compared to participants' values.

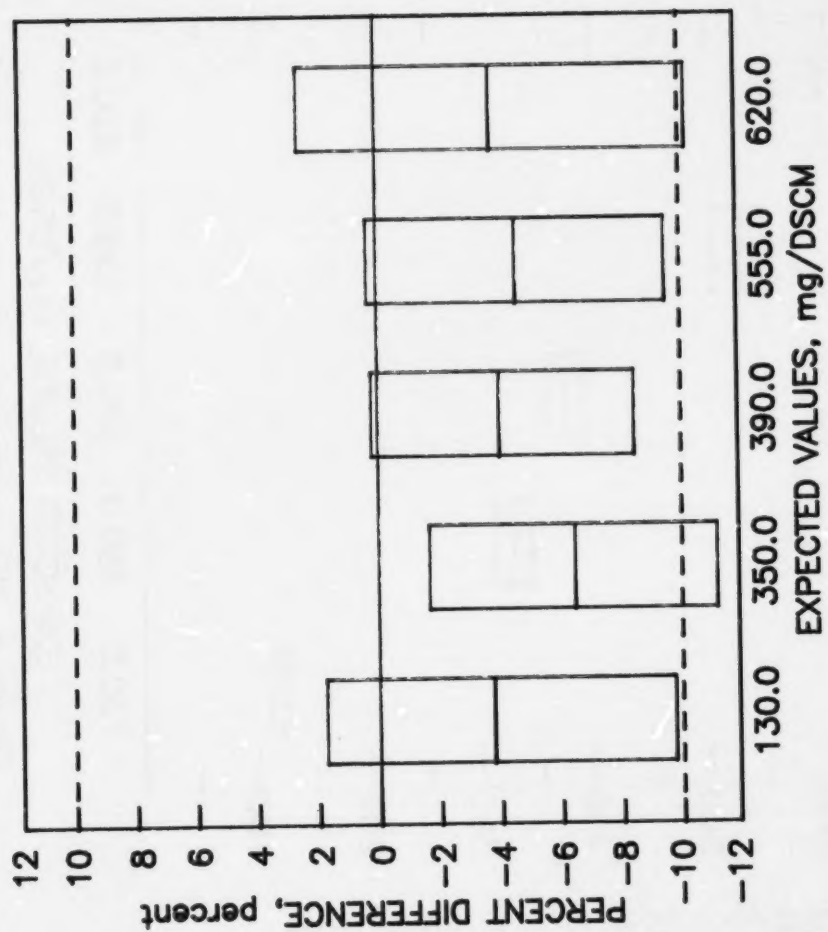


Figure 7. Percent difference of mean values and confidence intervals from expected values.

SECTION 7

METHOD 19 AUDIT

Standards of performance for newer electric utility steam generators (Subpart Da of 40 CFR 60) allow coal sampling and analysis to serve as an acceptable method for determining sulfur concentration in the scrubber inlet flue gas. The coal audit checks participants' ability to analyze coal samples for sulfur, ash, moisture, and Btu content.

The coal audit samples consisted of two samples each with 50 grams (g) of 60-mesh coal but with different parameter levels. The following American Society for Testing and Materials (ASTM) procedures⁽⁷⁾ were recommended, but not required, for participants' use in analyzing the coal samples:

- ASTM D-3177 (Standard Test Method for Total Sulfur in the Analysis of Coal and Coke)
- ASTM D-3174 (Standard Test Method for Ash in the Analysis Sample of Coal and Coke)
- ASTM D-3173 (Test for Moisture in the Analysis Sample of Coal)
- ASTM D-2015 (Standard Test Method for Gross Calorific Value of Solid Fuel by the Adiabatic Bomb Method)

Participants measured the parameters and reported their results for moisture (%) on an as-received basis, and their results for sulfur (%), ash (%), and gross calorific value (Btu/lb) on a dry basis.

In both audits, 85 percent of the laboratories that received the audit package returned data. Eighty-two of the same laboratories participated in both audits and returned data. This was an increase from last year's audit. Table 14 shows the total number of laboratories requesting participation and the number that returned data for coal audits 0386 and 0986.

TABLE 14. COAL AUDIT PARTICIPANTS

Category	No. requesting samples		No. returning data	
	0386	0986	0386	0986
Contractors	50	51	39	43
Industry	42	46	38	42
Federal	0	0	0	0
State	11	11	11	11
Local	6	4	5	4
Total	109	112	93	100

Tables 15 and 16 summarize the coal audit results. The number of analyses is greater than the number of participants because some companies had more than one laboratory participating. Each laboratory received its own set of samples and was asked to analyze the samples in duplicate. Accuracies of 5 and 10 percent were chosen as the reporting criteria for each of the four parameters.

In the 0386 audit, 90 percent of the laboratories analyzed both sulfur samples and submitted results within 10 percent of the expected value. In the 0986 audit, 84 percent of the laboratories analyzed the sulfur samples within 10 percent of the expected values. Only 50 percent were within the 10 percent criterion for moisture in the 0386 audit, whereas 60 to 70 percent in the 0986 audit achieved within the 10 percent criterion for moisture. For the ash analysis and Btu content, 98 to 100 percent of the reporting laboratories submitted results within 10 percent of expected values for both sample concentrations.

Comparison of the 0386 audit to the 0986 audit shows an improvement in the latter audit for only the moisture parameters. In the 0986 audit, the sulfur and ash levels were considerably lower, therefore allowing a greater chance for error in compliance testing.

TABLE 15. SOURCE COAL AUDIT--0386

Expected value	No. of analyses*	Laboratories accurate within 5% (%)	Laboratories accurate within 10% (%)
<u>Sulfur</u>			
1.72	(1) 130	70.0	90.8
	(2) 126	69.0	92.9
3.54	(1) 130	75.4	94.6
	(2) 126	77.0	93.7
<u>Moisture</u>			
1.04	(1) 131	24.4	48.9
	(2) 126	35.7	53.2
3.93	(1) 131	27.5	53.4
	(2) 126	25.4	50.0
<u>Ash</u>			
11.65	(1) 130	94.6	100.0
	(2) 126	92.1	98.4
17.17	(1) 130	97.7	100.0
	(2) 126	96.8	100.0
<u>Gross Calorific</u>			
12412	(1) 126	96.8	100.0
	(2) 123	95.9	100.0
13684	(1) 126	99.2	100.0
	(2) 123	99.2	100.0

*Numbers in parentheses indicate first and second analyses.

TABLE 16. SOURCE COAL AUDIT--0986

Expected value	No. of analyses*	Laboratories accurate within 5% (%)	Laboratories accurate within 10% (%)
<u>Sulfur</u>			
1.26	(1) 135	63.0	88.9
	(2) 128	60.2	84.3
3.02	(1) 135	79.3	93.3
	(2) 128	81.3	90.6
<u>Moisture</u>			
1.89	(1) 135	44.4	68.9
	(2) 127	44.9	69.3
2.11	(1) 135	28.1	62.2
	(2) 127	28.3	61.4
<u>Ash</u>			
9.73	(1) 134	95.5	99.3
	(2) 126	96.8	99.2
12.29	(1) 134	94.0	98.5
	(2) 126	96.0	98.4
<u>Gross Calorific</u>			
13271	(1) 131	98.5	99.2
	(2) 125	99.2	100.0
13578	(1) 131	98.5	100.0
	(2) 125	99.2	100.0

*Numbers in parentheses indicate first and second analyses.

REFERENCES

1. U.S. Environmental Protection Agency. Standards of Performance for New Stationary Sources--Appendix A. Title 40, Part 60, Code of Federal Regulations.
2. Streib, E.W., and M.R. Midgett. A Summary of the 1982 EPA National Performance Audit Program on Source Measurements. EPA-600/4-83-049, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1984.
3. Streib, E.W., T.J. Logan, and M.R. Midgett. A Summary of the 1983 EPA National Performance Audit Program on Source Measurements. EPA 600/4-85-004, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1985. 38 pp.
4. Streib, E.W., T.J. Logan, and M.R. Midgett. A Summary of the 1984 EPA National Performance Audit Program on Source Measurements. EPA 600/4-86-005, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, February 1986. 34 pp.
5. Streib, E.W., T.J. Logan, and M.R. Midgett. A Summary of the 1985 EPA National Performance Audit Program on Source Measurements. EPA 600/4-87-001, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, February 1986. 37 pp.
6. Chauvenet, W. Manual of Spherical and Practical Astronomy: Volume II--Theory and Use of Astronomical Instruments (Method of Least Squares). J.P. Lippincott and Co., Philadelphia, Pennsylvania, 1863.
7. American Society for Testing and Materials. Annual Book of ASTM Standards--1984. Volume 5.05. 01-050584-13, American Society for Testing and Materials, Philadelphia, Pennsylvania.

APPENDIX
FREQUENCY DISTRIBUTIONS

27

Sample no.	No.	Min.	10%	20%	30%	40%	50%	60%	70%	80%	90%	Max.	Mean	Std. dev.
							CO ₂							
6000	111	0.00	0.00	1.67	1.67	3.33	3.33	5.00	6.67	8.33	11.67	70.00	6.68	10.53
							O ₂							
6000	111	0.00	0.00	0.00	1.00	1.00	2.00	2.00	3.00	4.00	8.00	44.00	3.33	6.21
							CO							
6000	73	0.00	1.00	2.00	4.00	7.00	8.00	9.00	10.00	16.00	19.00	110.00	11.77	17.82

TABLE 18. DGM FREQUENCY DISTRIBUTION OF ABSOLUTE PERCENT DIFFERENCE

Sample no.	Min.	10%	20%	30%	40%	50%	60%	70%	80%	90%	Max.	Mean	Std. dev.	Skewness	Median
552	0.0	0.3	0.7	1.2	2.0	2.5	3.0	3.8	5.0	7.2	93.6	3.9	7.7	9.05	2.5
549	0.0	0.3	0.7	1.2	2.0	2.5	3.0	3.8	4.8	7.2	25.4	3.4	3.9	-0.03	2.5
539	0.0	0.3	0.7	1.1	1.9	2.5	2.9	3.7	4.6	6.7	13.5	3.0	2.6	-0.18	2.5
533	0.0	0.3	0.7	1.1	1.8	2.4	2.9	3.5	4.5	6.4	11.4	2.9	2.4	-0.27	2.4
530	0.0	0.3	0.7	1.1	1.8	2.4	2.9	3.5	4.4	6.3	10.7	2.8	2.3	-0.36	2.4
528	0.0	0.3	0.7	1.1	1.8	2.4	2.9	3.5	4.4	6.2	10.3	2.8	2.3	-0.45	2.4
526	0.0	0.3	0.7	1.1	1.8	2.4	2.8	3.5	4.4	6.0	9.7	2.8	2.2	-0.53	2.4

TABLE 19. SO₂ FREQUENCY DISTRIBUTION OF PERCENT DIFFERENCE--NO OUTLIERS REMOVED

Sample no.	No.	Min.	10%	20%	30%	40%	50%	60%	70%	80%	90%	Max.	Mean	Std. dev.
1	91	0.00	0.23	0.44	0.83	1.15	1.49	1.99	2.59	3.14	5.65	67.91	4.17	9.67
4	91	0.07	0.39	0.64	0.94	1.13	1.37	1.69	2.40	3.22	5.88	91.08	5.21	14.61
5	93	0.10	0.30	0.46	0.83	1.00	1.38	1.79	2.20	3.03	6.75	43.78	3.37	6.57
6	92	0.00	0.18	0.30	0.72	0.82	1.02	1.62	2.07	3.01	5.38	80.38	3.51	9.44
8	90	0.00	0.26	0.63	0.86	1.20	1.57	2.28	3.36	4.33	10.09	121.27	5.10	14.13

TABLE 20. NO_x FREQUENCY DISTRIBUTION OF PERCENT DIFFERENCE--NO OUTLIERS REMOVED

Sample no.	No.	Min.	10%	20%	30%	40%	50%	60%	70%	80%	90%	Max.	Mean	Std. dev.
2	67	0.00	1.00	2.42	3.08	3.85	5.23	5.97	7.74	12.95	40.97	99.52	14.30	23.52
3	70	0.09	0.68	1.26	2.43	3.60	5.05	6.47	9.50	13.75	40.36	99.44	12.03	18.56
5	70	0.00	0.62	2.31	3.08	4.62	8.69	11.54	15.23	20.06	29.69	103.31	14.57	20.63
7	69	0.03	0.31	0.86	1.69	2.86	4.43	6.74	8.94	12.60	42.29	99.51	11.43	18.19
9	70	0.00	0.38	1.33	2.31	2.77	3.85	5.67	8.18	12.92	9.74	99.49	9.87	16.18

TABLE 21. NATIONAL COAL AUDIT FREQUENCY DISTRIBUTION OF ABSOLUTE PERCENT DIFFERENCES OF EXPECTED AND REPORTED VALUES - STUDY 0386

Sample no.	No.	Min.	10%	20%	30%	40%	50%	60%	70%	80%	90%	Max.	Mean	Std. dev.
								Sulfur						
5000	256	0.00	0.58	1.16	1.74	2.91	4.07	4.07	5.23	6.40	8.72	579.07	8.73	50.84
7000	256	0.00	0.28	1.13	1.41	1.69	2.54	3.11	3.95	5.37	7.34	57.34	3.99	6.16
								Moisture						
5000	257	0.00	1.92	3.85	4.81	7.69	9.62	12.50	15.38	21.15	31.73	138.46	14.91	18.93
7000	257	0.25	1.53	3.56	5.85	7.89	9.67	11.45	15.52	20.87	26.72	69.47	12.65	11.05
								Ash						
5000	256	0.00	0.34	0.77	1.12	1.46	1.80	2.32	2.83	3.61	4.38	13.65	2.28	1.88
7000	256	0.00	0.12	0.35	0.52	0.76	0.99	1.28	1.57	1.98	2.74	6.64	1.32	1.22
								Gross Calorific						
5000	249	0.01	0.05	0.12	0.21	0.32	0.45	0.57	0.69	0.87	1.38	6.52	0.65	0.83
7000	249	0.0	0.16	0.35	0.49	0.60	0.68	0.82	0.97	1.32	2.89	8.79	1.15	1.44

TABLE 22. NATIONAL COAL AUDIT FREQUENCY DISTRIBUTION OF ABSOLUTE PERCENT DIFFERENCES OF EXPECTED AND REPORTED VALUES - STUDY 0986

Sample no.	No.	Min.	10%	20%	30%	40%	50%	60%	70%	80%	90%	Max.	Mean	Std. dev.
								Sulfur						
6000	263	0.00	0.33	0.99	1.32	1.99	2.65	3.31	3.97	4.97	8.28	56.95	4.33	7.02
8000	263	0.00	0.79	1.59	2.38	3.17	3.97	4.76	6.35	7.94	10.32	671.43	11.64	59.26
								Moisture						
6000	262	0.00	0.53	1.59	3.17	4.23	5.82	7.94	10.05	13.76	21.16	5032.28	51.32	440.37
8000	262	0.00	1.90	3.79	5.21	6.16	8.06	9.95	11.85	15.64	24.64	4501.90	45.16	383.51
								Ash						
6000	260	0.00	0.24	0.57	0.90	1.14	1.38	1.63	1.95	2.52	3.42	75.67	2.35	6.82
8000	260	0.00	0.31	0.51	0.92	1.13	1.64	1.95	2.36	2.77	3.49	28.06	2.00	2.64
								Gross Calorific						
6000	256	0.00	0.07	0.14	0.19	0.24	0.30	0.37	0.44	0.59	1.11	14.18	0.54	1.08
8000	256	0.00	0.04	0.08	0.13	0.18	0.23	0.27	0.35	0.47	0.85	7.81	0.44	0.87